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Published in:
Journal of Physical Chemistry C

DOI:
10.1021/jp307892s

Publication date:
2012

THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

Electrochemical Switching of Conductance with Diarylethene-Based Redox-Active Polymers

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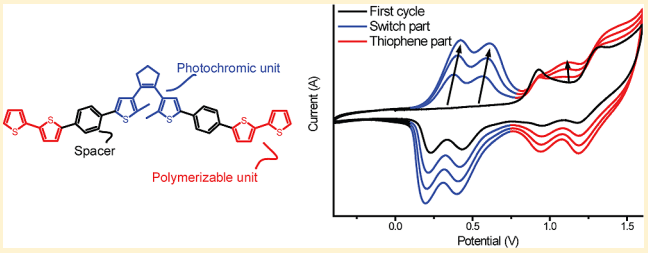
Supporting Information

ABSTRACT: Reversible switching of conductance using redox triggered switching of a polymer-modified electrode is demonstrated. A bifunctional monomer comprising a central electroswitchable core and two bithiophene units enables formation of a film through anodic electropolymerization. The conductivity of the polymer can be switched electrochemically in a reversible manner by redox triggered opening and closing of the diarylethene unit. In the closed state, the conductivity of the modified electrode is higher than in the open state.



INTRODUCTION

The development of smart interfaces, which respond to external input such as heat, light, and electrical stimuli, has received intense interest in recent years for applications as diverse as cell culturing,[1,2] droplet transport,[3] and increasingly in the development of organic electronics.[4−6] Light-switching within self-assembled monolayers (SAMs),[7−9] and in polymer films[10−12] has been demonstrated by several groups to date,[13,14] with azobenzene,[15] spiropyran,[16] and diarylethene[17] photochromic switches playing an important role as the photoresponsive elements in such systems.[18−20] A major challenge associated with the use of SAMs and thin (e.g., < 20 nm) polymer films in organic electronic devices, however, is that the magnitude of the change in conductance achievable is limited by the background tunneling current, which limits applications in organic-based devices. Nevertheless, recent progress has been made in addressing this issue,[21−24] and indeed switching of conductivity in SAMs have been reported also.[25−27] The use of thicker films will also overcome this, albeit at the cost of an increase in resistance and inhibition of photoswitching due to inner filter effects.[28]

Dithienylethenes have figured prominently in the development of switchable organic electronic devices, especially with regard to photoswitching of conductance, between the nonconjugated open and the conjugated closed forms.[18,29−31] Although mostly known as photochemical molecular switches, switching of dithienylethenes can also be achieved electrochemically.[32−37] Due to kinetic reasons, redox switching is essentially one way in solution. However, when immobilized on electrodes, both ring-opening and ring closing can be achieved electrochemically.[14,38−40] The difference in redox potentials between the open and closed states can potentially allow this class of molecular switches to function as active components in organic electronic devices, particularly in terms of switching of conductance.

Controlling the electrochemical response of electrodes through electrochemical modification using mono/multilayers of biphenyls has been demonstrated by McCreery and coworkers,[41] and with phenylbithiophenes by Lacroix and coworkers.[42] In these systems, electronic properties, including diode-like behavior, could be achieved with respect to redox active species in solution. The properties of the films once formed, however, are fixed, and although in many applications this is advantageous, exerting reversible control on the properties of the films after formation remains a key challenge.

Reversible electrochemical switching in polymer films was demonstrated recently by our group using thin polystyryl-dithienylethene films.[14] The use of styryl groups, however, limited the film thickness (<10 nm) and adhesive stability due to the nonconductive nature of the film formed at the potentials required for polymerization. However, when a bithiophene group is attached directly to the switching unit, excellent electropolymerization behavior is observed,[43] and, in contrast to the styryl-based system, film thickness was not limited by a lack of conductivity of the polymer at the potentials required for electropolymerization. In this latter system, in the ring-closed state, polymerization is not observed, and, although, in general, oxidation of the open form of a dithienylethene unit can lead to ring closure, polymerization was sufficiently competitive to allow for film formation. However, photo- or electrochemical switching in the polymer film formed did not occur, and the resulting polymer is best viewed as an alkene-

Received: August 8, 2012
Revised: October 3, 2012
Published: October 18, 2012

spaced polysexithiophene. An important goal therefore is to combine the dithienylethene redox switchable unit with a redox active polymer backbone that facilitates charge transport through the film without loss of the dithienylethene's switching functionality.[44] However, although redox-driven switching of conductance has been shown in monolayers and doped polymer films, reversible switching of conductivity in a polymer has, so far, not been demonstrated.

Here we show that reversible switching of conductivity within diarylethene-based redox-active polymer films is possible. This is achieved by combining a molecular switching unit, a dithienylethene, and an electropolymerizable bithiophene unit (Figure 1) without loss of redox switching

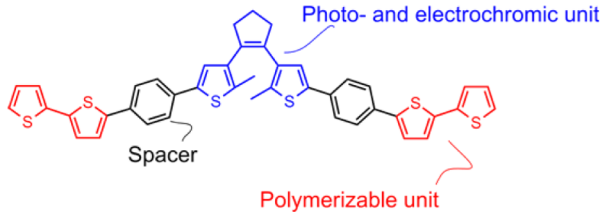


Figure 1. Bifunctional polymerizable dithienylethene switch **1o**.

properties both before and after electropolymerization. The key design aspect is the use of phenyl spacers. The phenyl groups are twisted out of plane, thereby limiting the electronic interaction between the switching unit and the polymerizable unit.[28,45] Although charge delocalization along individual polymer chains is reduced by using a phenyl spacer and hence impacts on intramolecular conductivity in the present system, conductivity is achieved by intramolecular charge migration through the polymer film, i.e., the system is a redox polymer.[46]

We demonstrate here that the polymer-modified electrode formed upon electropolymerization can undergo reversible redox driven switching between open and closed states of the dithienylethene under ambient conditions.

RESULTS AND DISCUSSION

Synthesis. The bifunctional monomer **1o** (Figure 1, where "o" indicates that the dithienylethene is in the open form) used to form the switchable electropolymer comprises of a central dithienylethene unit separated from the electropolymerizable units by phenyl groups. The monomer was prepared via Pd(0) catalyzed cross coupling of bis(*p*-bromophenyl)dithienylethene with 5-tributyltin-2,2′-bithiophene (see Supporting Information (SI) for details). In addition two model compounds bis(*p*-2-dithienyl)benzene (**2**)[47] and bis(5,5′-diphenyl)-dithienylcyclopentene (**3o**, Figure 2)[48] were prepared by reported procedures (see SI). The monomer **1o** is photoswitchable and shows electrochemical properties similar to that of the model compound **3o**. Irradiation of **1o** in CH_3CN at 365 nm results in a decrease in absorption at 365 nm and an increase in absorption at 550 nm, which is characteristic for ring closing of a dithienylethene switch. The absorption at 365 nm is partly due to the absorption of the bithiophene unit (vide infra, Figure 5).

Electropolymerization. Polymerization of **1o** and model compound **2** proceeds smoothly both potentiostatically and by cyclic voltammetry on Au disk/bead, Pt disk, indium tin oxide (ITO), and glassy carbon (GC) electrodes, under ambient conditions without the need to exclude water or oxygen and

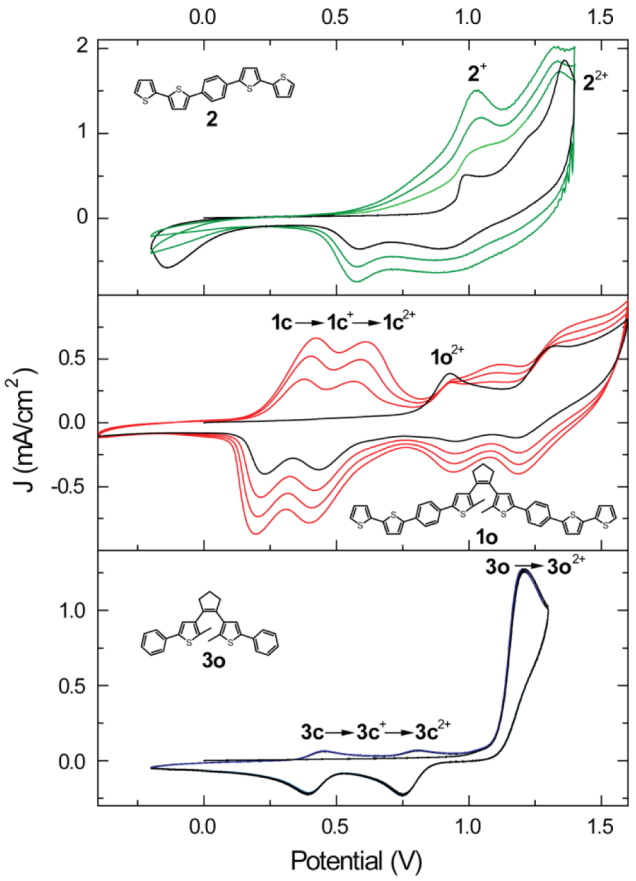


Figure 2. Multicycle cyclic voltammetry of **1o** (middle) shown together with model compounds **2** (top) and **3o** (bottom) {in 0.1 M $TBAPF_6$ in CH_2Cl_2, GC WE, Pt-wire CE and SCE RE}. In each case, the first cycle is shown in black (initial potential and scan directions are 0.0 V and positive, respectively).

without addition of Lewis acids. The polymer coatings formed are mechanically stable and can be stored in air under ambient conditions for at least several weeks without significant changes in their cyclic voltammetry.

The cyclic voltammetry of **1o**, **2**, and **3o** are shown in Figure 2. Upon electropolymerization of **1o**, two oxidation waves at 0.9 and 1.2 V are observed in the first cycle (shown in black in the cyclic voltammetry). On the return scan, however, four reduction waves are observed within the same potential window. In the second cycle, four reversible oxidations are observed, at 0.4, 0.6, 1.0, and 1.3 V.

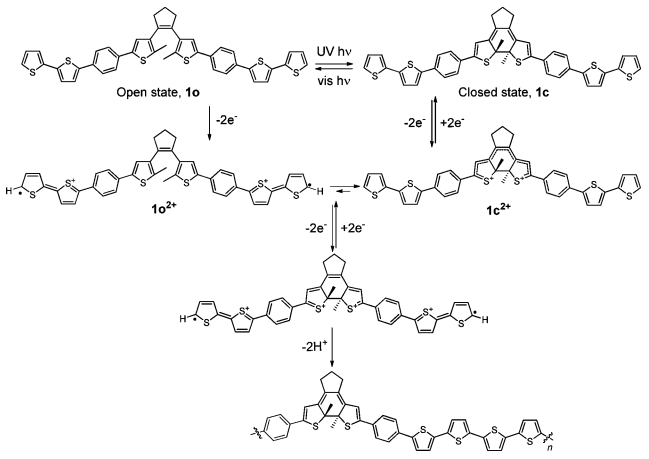
When comparing the electrochemistry of **1o**, **2** and **3o**, it is apparent that the cyclic voltammetry of **1o** appears to be a superposition of the voltammetry of **2** (irreversible oxidation of the bithiophene units at 0.9 V, followed by oxidative coupling) and **3o** (irreversible oxidation of the dithienylcyclopentene core at 1.2 V).[34] Counterintuitively, however, oxidation of **1o** to $\mathbf{1o}^{2+}$ at 0.9 V is followed by ring closure, to form $\mathbf{1c}^{2+}$ (where "c" indicates that the dithienylethene is in the closed form). For **3o**, oxidation at 1.2 V is required to achieve oxidative ring closing of the dithienylcyclopentene. Furthermore, the onset potential for electropolymerization for **2** is 1.0 V, while for **1o** electropolymerization does not occur until 1.2 V (see SI). With the exception of the first cycle, the electropolymerization of **1c** is essentially identical to that of **1o** (see SI).

Mechanism of Electropolymerization. The unusually high overpotential for the onset of electropolymerization is

dx.doi.org/10.1021/jp307892s | J. Phys. Chem. C 2012, 116, 24136−24142

rationalized in Scheme 1. The first oxidation process (0.9 V) observed for **1o** involves the peripheral bithiophene units,

Scheme 1. Mechanism for Electropolymerization of *bis*(Bithiophene) Functionalized Dithienylcyclopentene 1o/1c



which is followed by intramolecular electron transfer to the dithienylethene switching unit and subsequently ring closing to form $\mathbf{1c}^{2+}$. This conclusion is consistent with the electrochemistry of other dithienylethene switches bearing redox active side groups.[35,49] For **1c**, the first and second oxidation processes are dithienylcyclopentene centered (Figure 2), and hence oxidation of either **1o** or **1c** at <1.2 V results in the formation of $\mathbf{1c}^{2+}$, with electrostatic interactions with the bithiophene units shifting their oxidation potential to >1.2 V (see SI for details).

A redox copolymer of repeating tetrathiophene-phenyl-dithienylcyclopentene-phenyl units is formed upon multicycle cyclic voltammetry of **1o**. The dithienylcyclopentene component of the polymer is in the ring closed state after electropolymerization (poly-**1c**, Scheme 1). The cyclic voltammetry of the poly-**1c**-modified electrode in monomer free solution is shown in Figure S11 (SI). Two well-defined reversible oxidation waves are observed at potentials similar to those of **1c** in solution (Figure S11). Additional redox processes are observed at higher potentials that correspond to those of polythiophenes,[50] as observed for poly-**2**.

Electrochemical Switching. The switching of the polymer-modified electrodes from poly-**1c** to poly-**1o** and vice versa could be achieved electrochemically (Figure 3). This can be monitored, without switching the material, using cyclic voltammetry, by cycling between 0.0 and 0.5 V, since ring-opening is a relatively slow process, as shown earlier for dithienylethene-based SAMs and polymers.[14,31,38] In this range, the poly-**1c**/poly-$\mathbf{1c}^{+}$ redox process is observed. In the open state, the Faradaic current is negligible compared to that in the closed state. Importantly, the tetrathiophene units formed in the electropolymerization are conductive upon doping at potentials intermediate of the open and closed states of the dithienylcyclopentene core, thereby enabling switching of conductivity potentiostatically through the whole film regardless of thickness.

From the closed polymer (poly-**1c**), spontaneous ring-opening to the open polymer form (poly-**1o**) is observed after several hours, depending on polymer film thickness, due to the presence of trapped charges within the film.[51,52] The ring-

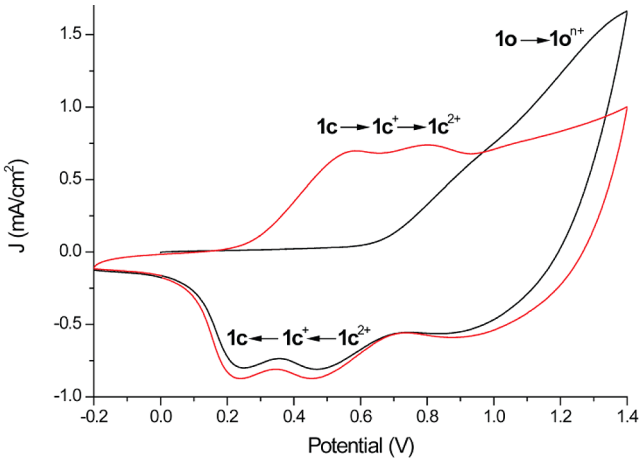


Figure 3. Electrochemical switching: ring closing of the dithienylcyclopentene unit of poly-**1o** to poly-**1c** (conditions as for Figure 2, in monomer-free solution; initial scan shown in black).

opening was manifested in a disappearance of the redox waves at 0.3 and 0.6 V (i.e., the oxidation of **1c** to $\mathbf{1c}^{+}$ and $\mathbf{1c}^{2+}$, respectively) and an increase in the intensity of the oxidation waves above 0.8 V. Cyclic voltammetry between −0.2 and 1.4 V resulted in ring closure to restore the closed polymer poly-**1c** (Figure 3), as observed for the monomer when electropolymerizing with the open form (vide supra).

Electrochemical ring-opening was also achieved by holding the film at ca. 0.35 V or by repeated cyclic voltammetry between −0.4 and 0.4 V (Figure 4), i.e., only sufficiently positive to form poly-$\mathbf{1c}^{+}$, as shown previously for monolayers of dithienylethenes.[38,40] Multiple switching cycles were performed (Figure 4). Holding the potential at 0.0 V for an equal period of time did not result in changes to poly-**1c**. On the basis of the fact that a decrease in signal intensity with cycle number is observed in both the switching and the control experiment, this is ascribed to gradual dissolution of the polymer into the solvent.[53] A change in morphology during swelling and shrinkage of the polymer is commonly observed for organic semiconductive polymers.[54] The gradual decrease in response is likely to be solved by application in a solid state device.

Spectroscopic Properties. Diarylethene switches undergo substantial changes in their UV/vis absorption spectra upon switching as observed for monomer **1o** in solution (vide infra, Figure 5). Similarly, a change in the UV/vis absorption spectrum of poly-**1o** was observed upon electrochemical ring closing of the dithienylethene units in the polymer (Figure 5), confirming that the diarylethene unit undergoes ring closure also.

The polymer films were characterized by Raman spectroscopy. At λ_{exc} 785 nm, resonance enhancement is expected for the polaronic states (as observed before for a related sexithiophene polymer).[52] Spectro-electrochemistry reveals the changes in the resonance Raman spectra as the potential is varied (Figure 6). The resonance enhancement of Raman scattering from either the central switch unit or of the tetrathiophene unit in the polymer can be expected depending on the localization of the polarons. At all potentials greater than 0.3 V, the band at 1605 cm^{-1}, which is characteristic of a phenyl ring, is strongly enhanced. The broad band at 1440 cm^{-1} persists at all potentials also, and is characteristic of the C═C symmetric stretch in the oxidized thiophenes. At potentials

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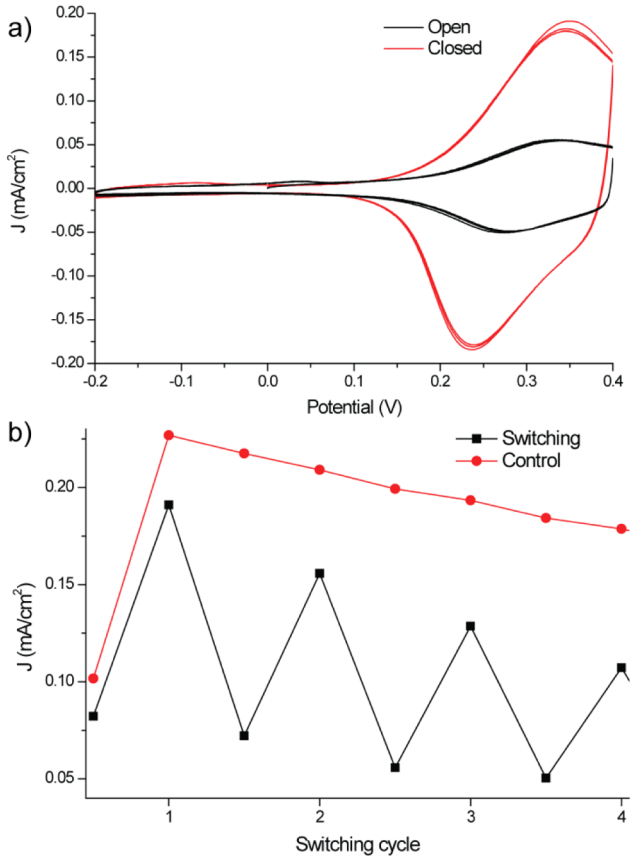

Figure 4. (a) Cyclic voltammetry between −0.2 and 0.4 V showing the first oxidation wave of poly-**1c**. (b) Repeated switching between poly-**1c** and poly-**1o**. Ring-opening was achieved potentiostatically at 0.35 V (15 min) and closing by a single cycle between −0.2 and 1.0 V. The $I_{p,c}$ at 0.3 V after each step is shown in black. The red line shows the change in $I_{p,c}$ at 0.3 V when the potential used was 0.0 V (over 15 min).

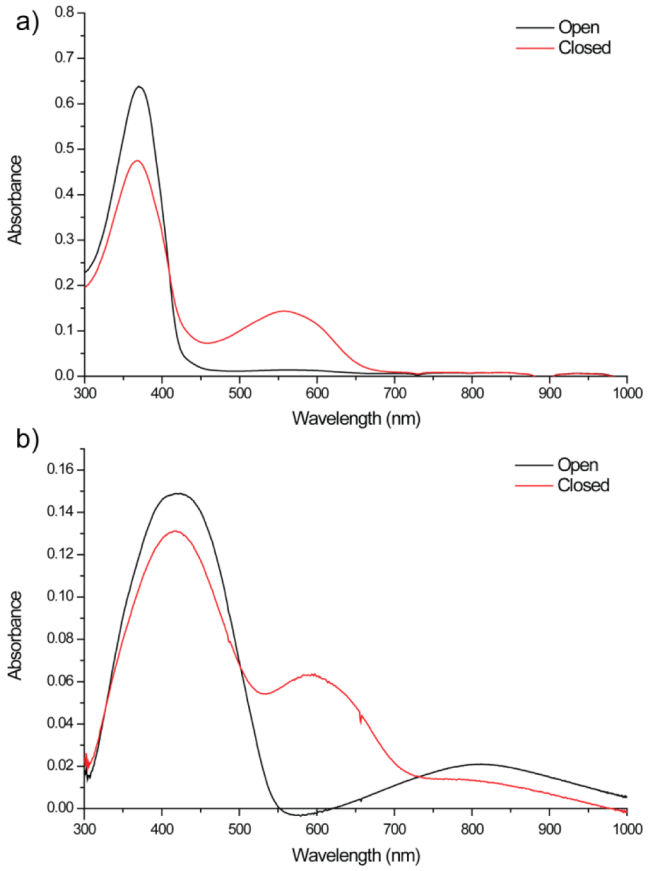

Figure 5. UV/vis absorption spectrum of (a) **1o** (black) and **1c** (red) in CH_3CN and (b) poly-**1o**/**c** on an ITO electrode (dry slide). (Black is ring opened, red is after electrochemical ring-closure.)

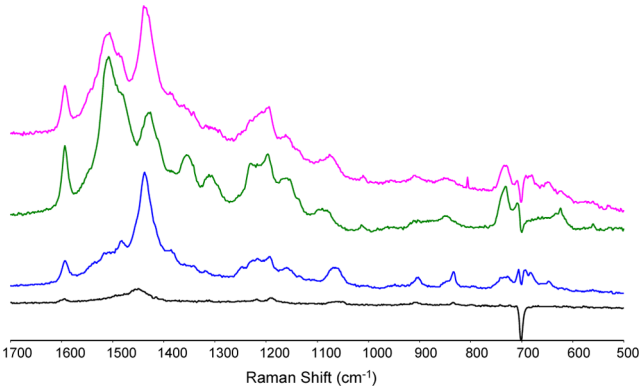

Figure 6. Spectroelectrochemistry of the polymer on a gold bead electrode, λ_{exc} = 785 nm, at 0.3 V (black), 0.7 V (blue), 1.1 V (green), and 1.4 V (pink).

above 0.7 V, additional bands assignable to the tetrathiophene mono/bipolaron are observed at 1160 cm^{-1}, 1195 cm^{-1}, 1230 cm^{-1} and 1505 cm^{-1}. The absence of these vibrations below 0.7 V is consistent with the assignment of the redox processes below 0.7 V as being centered on the dithienylethene unit.

Film Conductivity. The cyclic voltammetry of decamethylferrocene, which shows a reversible redox couple at −0.1 V, was used to demonstrate the effect of switching on the conductance of a poly-**1c**/poly-**1o**-modified electrode. The cyclic voltammetry of decamethylferrocene in solution using an unmodified electrode (inset) and a polymer-modified electrode in both the open (red line) and closed (blue line) states is shown in Figure 7. Despite oxidation of decamethylferrocene being 0.5 V lower than the oxidation potential of the closed state polymer film, a clear difference is observed between the cyclic voltammetry of decamethylferrocene upon switching the electrode from poly-**1c** state to the poly-**1o** state. In the open state, the redox chemistry of decamethylferrocene is blocked at potentials below 0.3 V. Upon ring closing, by a single cycle between 0.0 and 1.2 V, the conductivity of the polymer film is increased, and a substantial increase in decamethylferrocene signal is observed. This shift in redox potential demonstrates electrochemically driven switching of the conductance of the electrode.

To further characterize the change in conductivity upon switching, in situ conductivity measurements were performed using interdigitated microelectrode arrays (IDAs). Polymerization was performed using cycling voltammetry at a low scan rate (Figure 8) until a relatively homogeneous coverage of the electrodes was observed by optical microscopy (see SI). Initially, upon polymerization the current at both electrodes is equal. However, once a connection between the electrodes is made, clear changes between the source and drain currents can be observed, where the anodic current is higher at the second electrode and the cathodic current is higher at the first electrode, i.e., source-drain behavior (Figure 9).[55]

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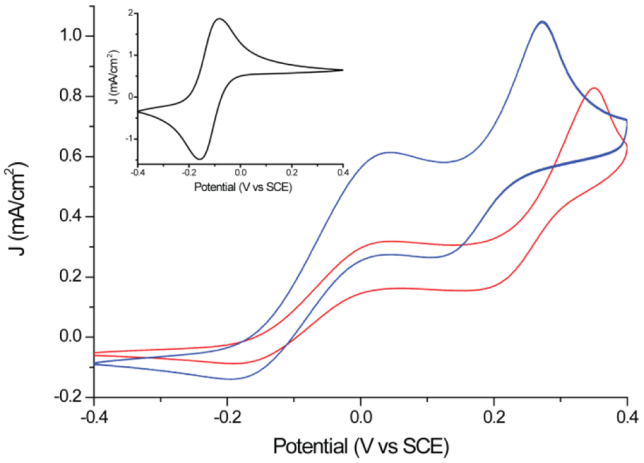

Figure 7. Cyclic voltammetry of decamethylferrocene (inset: unmodified GC electrode with decamethylferrocene) on red: poly-**1o**; blue: poly-**1c** modified electrodes).

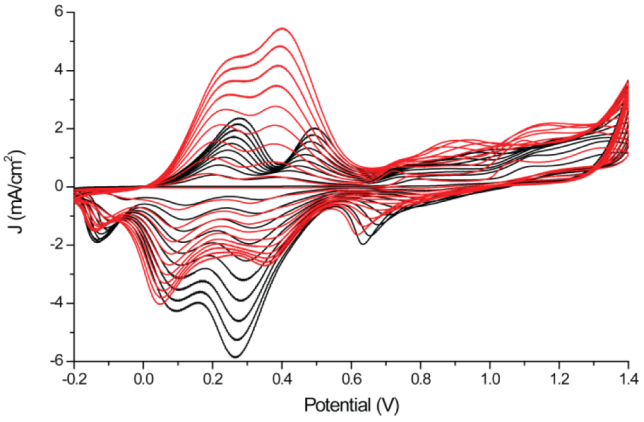

Figure 8. Polymerization on an IDA using cyclic voltammetry: electrode 1 (black); electrode 2 (red). Source drain offset = 20 mV; scan rate is 0.05 V s^{-1}.

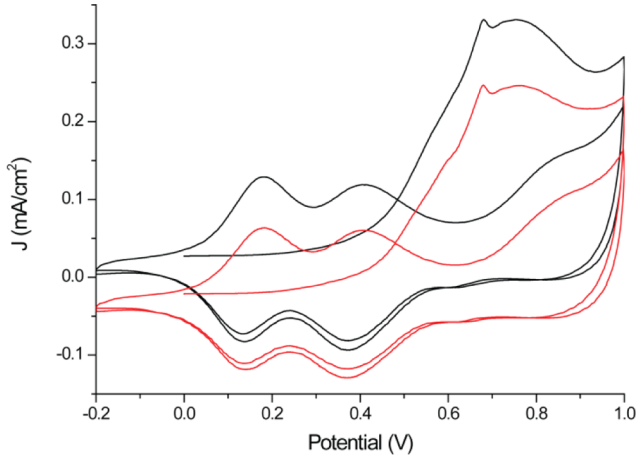

Figure 9. Electrochemical ring-closing on an IDA. Both electrodes are cycled with the same scan rate and in the same potential window. Scan rate = 0.1 V/s, no source drain offset, electrode 1 (black), electrode 2 (red).

Measurements carried out at scan rates higher than 0.1 V s^{-1} show a difference between the open and closed state in the potential window of −0.2 to 0.4 V vs the saturated calomel electrode (SCE) (Figure 10). However, analysis of the polymer formed on an IDA with a source/drain offset of 10 mV at low

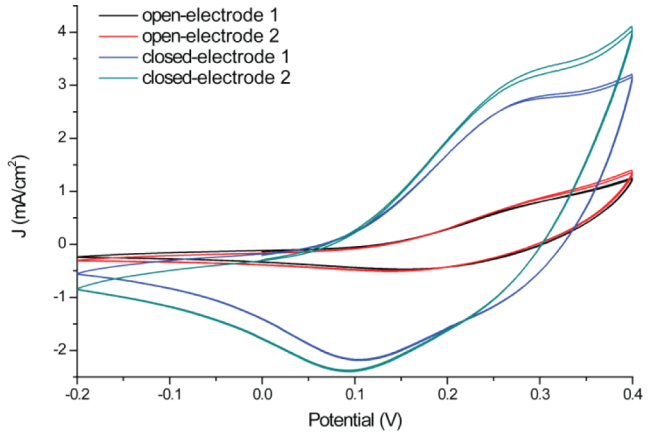

Figure 10. In situ conductivity measurement on a polymer-coated IDA. Differential scan, source drain offset 10 mV, scan rate 0.1 V/s, counter electrode = Pt, reference electrode = $Ag/AgNO_3$ (in ACN).

scan rates (5 mV s^{-1}) resulted in spontaneous ring-opening on a much shorter time scale than observed on macro electrodes (vide supra). This is due to the occurrence of electrochemical ring-opening occurring faster than the time scale of the measurement. Since the data required to determine in situ conductivity can only be obtained using low scan rates, this precludes accurate determination of the conductivity of the polymer in the closed state. Measurements performed at faster scan rates did show significant differences in source-drain behavior between the open and the closed form. This is depicted in Figure 10. Although at these scan rates the conductance of the polymer film cannot be calculated since the measured current is mainly faradaic, lateral current is observed for the closed polymer film and not for the open polymer film. This demonstrates an increase in conductivity upon ring-closing.

CONCLUSION

Here we have described a new polymeric functional material based on a bifunctional monomer in which the electropolymerizable groups are separated from the photochromic unit by phenyl spacers. The polymerization can be carried out under ambient conditions. It is shown that both units retain their functionality with redox-driven switching achieved in the polymer-modified electrodes. The phenyl spacer is a key design component, as it serves to separate the functionalities of the two functional components: the central switch unit and polymerizable bithiophene units. Upon switching of the polymer to the open form, the conductivity of the polymer films at potentials below 0.8 V decreases. The redox-driven switching of the conductance was demonstrated by using a modified electrode to analyze the well-known redox couple of decamethylferrocene, and the behavior of the polymer in both open and closed states was probed using IDAs.

The observed redox-driven switching in conductivity of the polymer after formation is in contrast with previously reported systems in which the properties of the polymer were controlled solely in the preparation stage[41,42] or which employ photochemically induced changes.[16] A key challenge in organic electronics is not to simply duplicate the functions achieved

dx.doi.org/10.1021/jp307892s | J. Phys. Chem. C 2012, 116, 24136−24142

already with nonmolecular materials, but instead to introduce new behavior: in the present case, the ability to switch conductivity reversibly between two states using electrochemical stimulus. This holds considerable advantages in terms of application compared with optically switched systems, as it obviates the need for optical access to an organic electronic device. Furthermore, the electropolymerization and the polymer formed is not especially sensitive to oxygen or moisture, which facilitates application and opens new opportunities in the use of dithienylethene switches as electrochemically switchable components in closed electronic devices where the delivery of optical stimuli is not possible.

■ ASSOCIATED CONTENT

Supporting Information

Details of synthesis and characterization of compounds **1**−**3** and methods and additional electrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The Netherlands Organization for Scientific Research (NWO, VIDI 700.57.428; H.L., W.R.B.), the European Research Council (Advanced Investigator Grant 23849; P.d.M., B.L.F.) and the Ubbo Emmius fund (J.A.) are acknowledged for financial support.

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